

UNPUBLISHED PRELIMINARY DATA

## STRESS CORROSION CRACKING OF TITANIUM ALLOYS

PROGRESS REPORT: APRIL 1 - JUNE 30, 1964

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by

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# ABSTRACT

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This report describes results of the first quarter of research work to determine the mechanism of hot-salt stress corrosion cracking of titanium alloys. Exploratory tests were started with radiotracer  $^{36}\text{Cl}$  to determine the role of chloride in the corrosion cracking phenomenon. Direct observations were made of salt reaction with Ti-8Al-1Mo-1V alloy at various temperatures. Electron microscopy studies were started to determine the relationship between alloy structure and crack morphology. Preliminary results indicate that a small amount of HCl gas is given off during dehydration of sea salt heated to 650°F. The HCl gas and/or resultant hydroxides may be involved in initiation of stress corrosion cracking. Examinations of cracks revealed that:

- Cracks propagate along alpha phase grain boundaries and alpha-beta phase interfaces.
- Cracks appear to propagate by chemical attack with no evidence of mechanical rupture.
- The beta phase is cathodic to the alpha matrix and is contained unattacked within corrosion products in stress corrosion cracks.

Author

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## INTRODUCTION

This is the first quarterly progress report of NASA-sponsored research by the Savannah River Laboratory on the mechanism of hot-salt stress corrosion cracking of titanium alloys. Incomplete or unconfirmed data may be presented in these progress reports.

The objective of this research is to develop fundamental knowledge about the corrosion phenomena involved in cracking. The material-metallurgical factors and the chemical-environmental factors that affect susceptibility to cracking are to be investigated for both low temperature (wet) and high temperature (wet and dry) conditions, with emphasis on the latter. The exact roles of chloride ions, chlorine gas, oxygen, hydrogen, and water in the corrosion phenomena will be investigated as well as the effects of fabrication, heat treatment, welding, and surface conditions.

## SUMMARY

During this first quarter supplies were procured, test equipment was set up, and exploratory tests were started with radiotracer  $^{36}\text{Cl}$  to determine the role of chloride in hot-salt corrosion of Ti-8Al-1Mo-1V alloy. Electron microscopy studies were started to determine the microstructure and the substructure of the alloy, and to examine the morphology of stress corrosion cracks. Thin-foil transmission electron micrographs will be used to determine the structure, and replication of crack-fracture surfaces and metallographic cross sections will be used in the morphology examinations.

Preliminary results indicate that a small amount of HCl gas is given off initially when sea salt is heated to about 650°F. Tests are continuing to determine if either the HCl gas or metal hydroxides remaining in the salt are involved in initiation of stress corrosion.

Deposits of sea salt containing radiotracer  $^{36}\text{Cl}$  produced tiny corrosion pits and cracks in the surface of an alloy sample that was stressed to 144,000 psi and heated for one week at 650°F. When the salt was washed off, only traces of radioactivity remained. Microautoradiographs are being prepared to determine if chlorides are concentrated at sites of stress corrosion.

Crystals of dried sea salt were clamped between the faces of Ti-8Al-1Mo-1V alloy strips that had metallographically polished edges. Individual "salt sandwiches" were heated for 8 hours at temperatures ranging from 400 to 1200°F. At temperatures  $\geq$  800°F, corrosion products spread from the salt-metal interface across the polished edges. Efforts are being made to identify the corrosion products.

Electron microscopy of a U-bend sample of the alloy that had cracked by hot-salt exposure revealed that:

- Cracks propagate along alpha phase grain boundaries and alpha-beta phase interfaces.
- Cracks appear to propagate by chemical attack with no evidence of mechanical rupture.
- The beta phase is cathodic to the alpha matrix and is contained unattacked within corrosion products in stress corrosion cracks.

Thin foils of mill-annealed alloy were successfully prepared for electron transmission studies of fine structure.

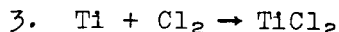
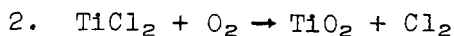
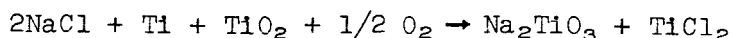
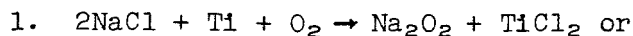
## DISCUSSION

### BACKGROUND

Titanium alloys are prime candidates for use in the construction of supersonic transport aircraft (SST). The alloys are known to be susceptible to stress corrosion cracking when in contact with chloride salts at temperatures above about 550°F. Skin temperatures may exceed this limit during operation of the SST, and salt contamination is likely to occur during landing and take-off from seacoast airports.

The 550°F threshold temperature for the hot-salt cracking phenomenon was established by past research. The time to initiate cracking decreases with increasing stress and temperature. Unpublished research results indicated that chloride salts of other cations or mixtures of various chlorides can cause cracking at temperatures lower than 550°F.

Chemical reactions that have been proposed previously for hot-salt corrosion of titanium alloys involve the formation of titanium dichloride then chlorine gas. Once started, these reactions could be autocatalytic, as follows.



4. (Repeat reactions 2,3; 2,3; etc)

The purpose of the current research at SRL is to determine whether these proposed reactions are valid, and whether or not other reactions involving  $\text{H}_2\text{O}$  or  $\text{H}_2$  contribute to cracking.

## PROCUREMENT

Arrangements were made with Langley Research Center to obtain a 0.050-inch-thick sheet of Ti-8Al-1Mo-1V alloy from the same lot of material being used in their research. Pending receipt of this material, tests were begun using a 0.032-inch-thick sheet of the alloy previously purchased from Titanium Metals Corporation of America.

Radioactive sea salt was prepared from radiotracer  $^{36}\text{Cl}$  (as 1M HCl) purchased from Oak Ridge National Laboratory. The HCl tracer solution was added to natural sea water in the ratio of 1 to 50 parts by volume, and the pH of the sea water was adjusted to the original level with sodium hydroxide. The sea water was then evaporated to make dry salt. The beta radiation activity of this salt was  $3.5 \times 10^7$  disintegrations per minute per gram of salt.

Oxygen-18 (92.8% isotopic purity) was purchased for tests to determine the roles of atmospheric oxygen and  $\text{TiO}_2$  in the corrosion phenomenon. This material was not delivered soon enough to begin tests this quarter.

## EXPERIMENTAL RESULTS

### Role of Chlorine

Radioactive sea salt is being used to determine whether chlorine gas or any volatile chlorine-bearing product is formed by reaction of hot salts with Ti-8Al-1Mo-1V alloy. Preliminary results, described below, indicate that a small amount of HCl gas is given off during dehydration of sea salt heated to 550 to 650°F. The HCl gas may be involved in initiation of stress corrosion cracking.

Samples of radioactive salt alone and salt-coated chips of the alloy were heated in a tube furnace at up to 650°F. Air was passed through the furnace (at 0.1 to 0.4 cubic feet per hour) and through a beta radiation air monitor. Significant radioactivity ( $^{36}\text{Cl}$ ) was not detected in the air during 3 hours of heating below 650°F. Released radioactivity was detected when samples of salt and salt-coated alloy chips were heated to higher temperatures.

Subsequent tests showed that the release of radioactivity from the salt alone stopped after about 3 hours at temperature, and after about 10 to 30 minutes from salt-coated chips of alloy. It is not clear whether the more rapid release of activity from the salt-coated chips was due to a metal-salt reaction or to the increased ratio of surface area to volume of salt.

Two additional experiments were performed to demonstrate that the chlorine-bearing volatile product was HCl gas. In the first experiment a sample of salt-coated chips of alloy that had been heated at 650°F was cooled to room temperature, and three drops of water were added. When reheated to 650°F, this sample again released a radioactive product over a brief period. In the second experiment a sample of alloy chips coated with nonradioactive sea salt was heated at 650°F, and the effluent air was bubbled through a water bath. The water bath was then analyzed and found to contain 11 ppm chloride ion and only traces of cations such as Na, Mg, etc. Taken together, these results indicate that HCl gas is liberated during dehydration of the salt. Experiments are continuing to make certain the volatile chlorine-bearing compound is HCl and to determine whether stress corrosion cracking is initiated by release of HCl from the hot salt.

A series of tests was conducted to determine if chloride is concentrated in the surface oxide film and/or the corrosion products at sites of stress corrosion cracking. Deposits of radioactive sea salt were placed on test strips, which were then stressed to approximately 90,000 psi and heated for one week at 650°F. Samples of the alloy with different surface conditions were tested (Figure 1). After hot-salt exposure, the salt was rinsed off and the samples were scanned in a beta radiation counter. Traces of radioactivity were detected on each sample (Figure 2), but no significant concentration of chloride was indicated in the surface oxide. Tiny cracks and pits (visible at magnifications of 10X and higher) were observed around the edge of the salt-coated area on one sample that had been polished through 6-micron diamond abrasive prior to salt exposure (Figure 3). They did not occur where the salt deposit was thickest, which is in agreement with observations by other workers and suggests that atmospheric oxygen may be involved.

The time required for initiation of the observed corrosion pitting and cracking has not been determined, but the attack may start very early in the hot-salt exposure. If HCl gas is given off during salt dehydration, some sodium hydroxide must be produced in the salt. Either the HCl or the NaOH may cause the initial attack. Experiments are continuing to determine how the corrosion is initiated.

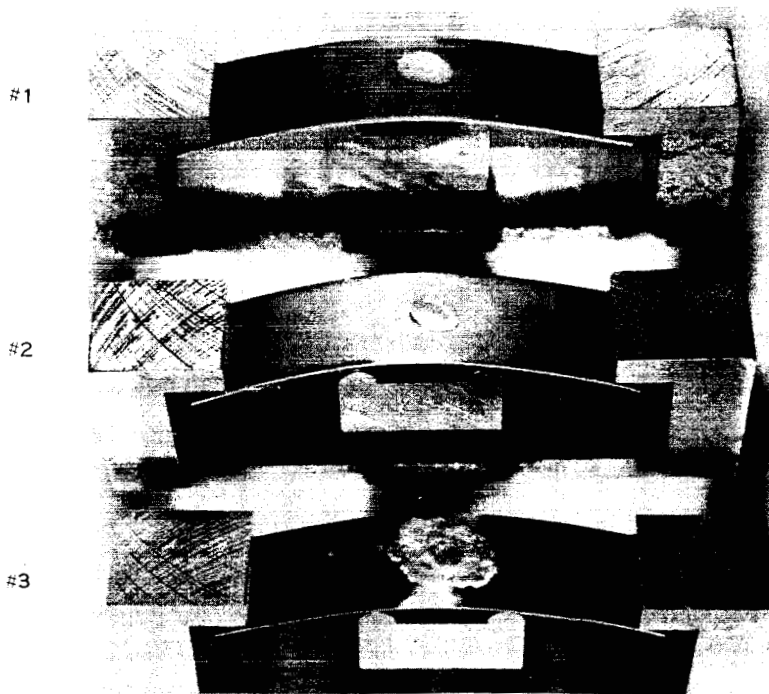


FIGURE 1. SAMPLES OF Ti-8Al-1Mo-1V ALLOY (with deposits of radioactive sea salt) STRESSED TO APPROXIMATELY 144,000 PSI AND HEATED FOR ONE WEEK AT 650°F 1X

Sample surfaces were prepared as follows:

- #1 As-rolled, chemically cleaned with standard procedure\*.
- #2 As-rolled, chemically cleaned with standard procedure except time in  $\text{HNO}_3$  was 10 min.
- #3 As-rolled, mechanically polished through 6-micron diamond abrasive.

\*Standard cleaning procedure:

- (a) Clean with acetone and cloth
- (b) Immerse in NaOH base cleaner (6 oz. NaOH per gallon of water) at 300°F for 10 minutes
- (c) Rinse in hot water
- (d) Dip in 20% nitric acid solution for 30 seconds
- (e) Rinse thoroughly in water and dry



0	2	0
3	1	0
4	5	0
0	2	3
3	0	4
11	14	7
16	8	4
10	4	0
9	7	0
0	9	0
0	0	0
5	3	0

FIGURE 2. RESIDUAL BETA ACTIVITY AFTER SEA SALT CORROSION

Counts per minute over 3-minute counting period on samples shown in Figure 1. Shaded areas indicate salt deposits which were rinsed off prior to counting.

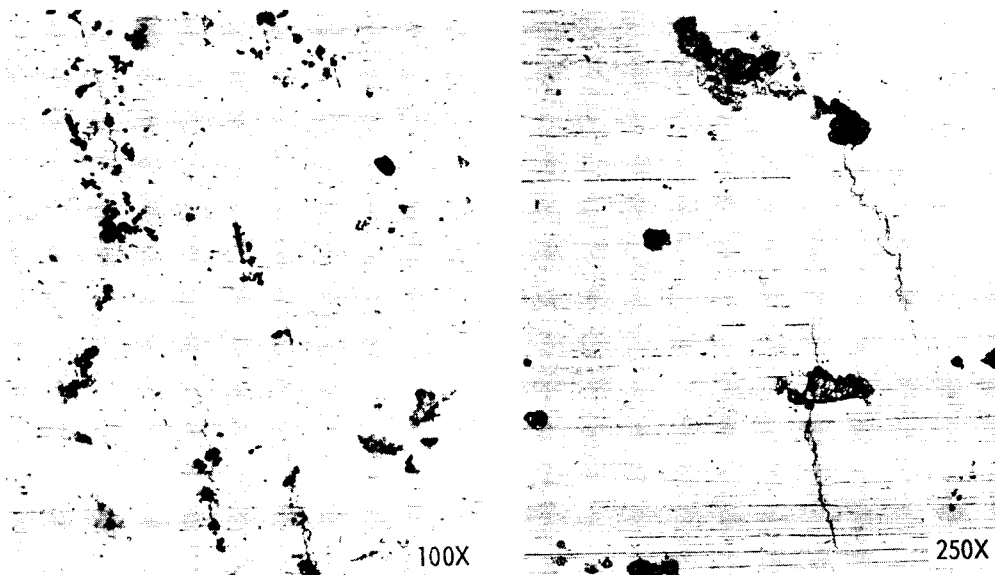


FIGURE 3. PITTING AND CRACKING CAUSED BY SEA SALT ON STRESSED Ti-8Al-1Mo-1V ALLOY (Sample #3, Figure 1)

#### • Direct Observation of Salt Corrosion

An unstressed wafer of the alloy was coated with natural sea salt and heated in an apparatus that permitted direct observation of the sample under a low-power microscope (up to 30X). No evidence of reaction was observed after 30 minutes at temperatures up to 650°F, but at 1000°F white and yellow reaction products were produced. Probing the reaction products with moist litmus (after cooling) indicated a pH of 8 to 10, which suggested that a hydroxide or an alkaline oxide was present.

In order to observe more closely the reaction at the salt-metal interface, crystals of dried sea salt were sandwiched between two strips of alloy sheet, the edges of which had been given a metallographic polish. The salt crystals were positioned flush with the polished edges of the strips, which were then bolted together with only enough force to hold the salt in place. These "salt sandwiches" were then heated for 8 hours at 400, 650, 800, 900, 1000, 1100, and 1200°F. Changes observed with the naked eye during these tests are described in the table on page 15. Figure 4 shows the samples after cooling to room temperature.

The "salt sandwiches" will be disassembled; half will be analyzed by X-ray diffraction, spectroscopy, etc, to attempt identification of corrosion products, and half will be used for metallography.

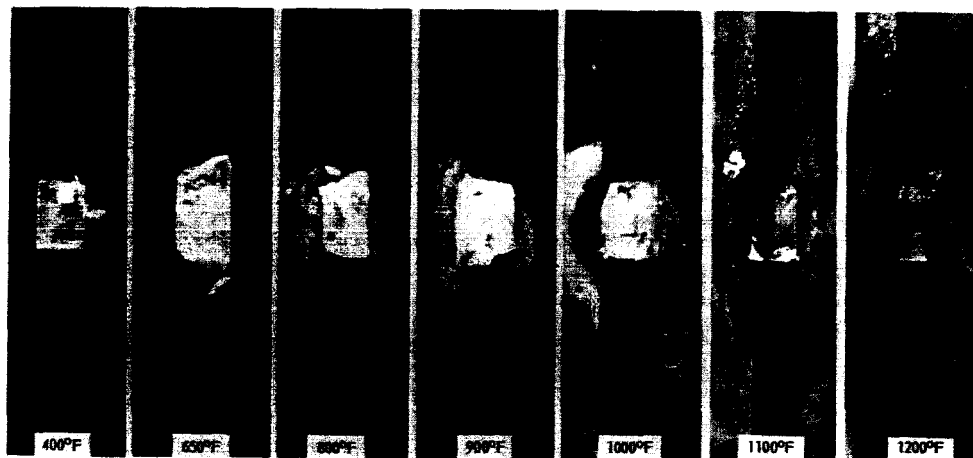


FIGURE 4. APPEARANCE OF TITANIUM - SEA SALT "SANDWICHES" 5X

Crystals of dried sea salt were placed between strips of Ti-8Al-1Mo-1V alloy and heated for 8 hours at indicated temperatures.

## Electron Microscopy Studies

Electron microscopy techniques are being used in hot-salt corrosion studies to determine whether a relationship exists between alloy substructure and susceptibility to stress corrosion. The nature of grain and phase boundaries is of particular interest because these boundaries have been shown to be susceptible paths along which stress corrosion cracks propagate in the alloy<sup>(1)</sup>.

During this quarter the following were accomplished:

- The substructures of the alloy in both the mill-annealed and duplex-annealed conditions\* were examined using the replication technique.
- One cracked U-bend sample was examined using replicas of sections through cracks and replicas of crack-fracture faces (fractography).
- Thin foils of the alloy in the mill-annealed condition were successfully prepared for electron transmission studies of fine structure.

The structures of the mill- and duplex-annealed alloy are shown in Figure 5. In both conditions, small particles of a second phase (presumably the body-centered cubic beta phase) were distributed within the alpha matrix and along grain boundaries. Many fine second phase particles were also seen in some of the alpha grains, but these finer particles were much more distinct in the duplex-annealed material (compare Figure 5b and c). The morphology of this fine precipitate indicates it is either needle-like or plate-like in character and precipitates on a definite habit plane. Evidently the duplex-annealing treatment caused precipitation of this phase within the alpha matrix.

The following observations indicate that both sizes of particles are cathodic to the matrix and that the interfaces between the particles and the matrix are probably involved in the cracking mechanism.

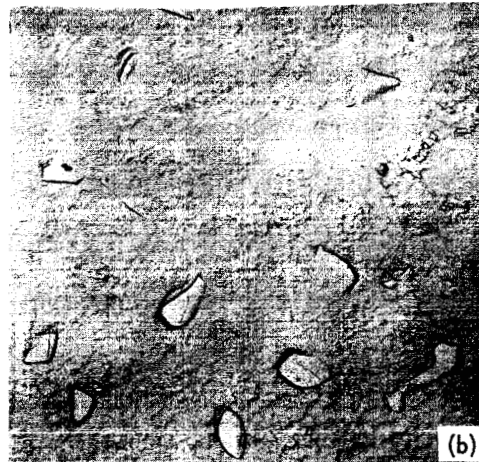
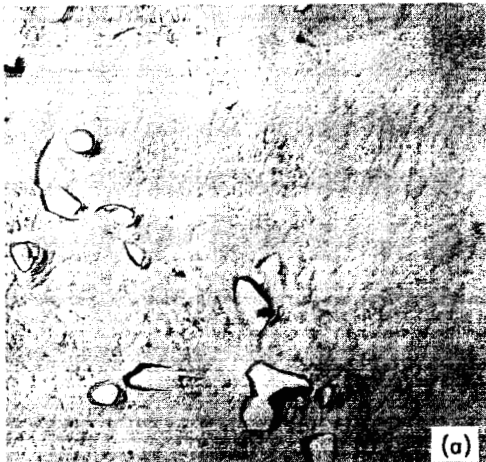
- Stress corrosion cracks propagate along the alpha-beta phase interface and along alpha grain boundaries.
- Preferential etching occurred at phase interfaces in metallographic samples.

\*Mill anneal: 1450°F, 8 hr, furnace cool

Duplex anneal: 1450°F, 8 hr, furnace cool  
1450°F, 1/4 hr, air cool

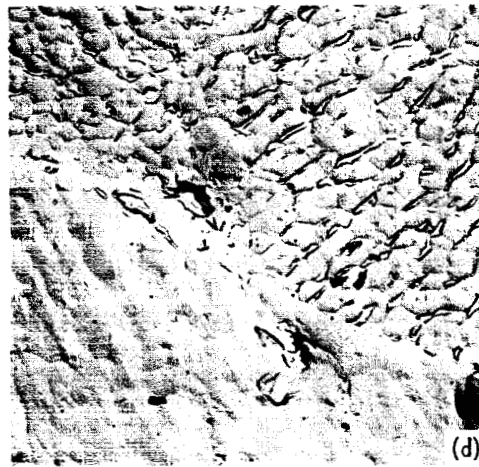
- Beta particles were contained, apparently unattacked, within corrosion products that filled stress corrosion cracks.

The last observation was made during examination of a U-bend sample of the alloy (in the mill-annealed condition) that had been coated with natural sea salt, stressed to the yield point, heated in air for 17 hours at 1200°F, then cooled to 650°F and held at that temperature for several days. Prior to exposure the structure was similar to that shown in Figure 5a and b. The exposure induced precipitation of the fine particles and produced a structure similar to that of duplex-annealed material (Figure 5c and d).



Structure in the mill-annealed condition

3,800X



3,600X

15,800X

Structure in the duplex-annealed condition

FIGURE 5. ELECTRON MICROGRAPHS OF Ti-8Al-1Mo-1V ALLOY

The exposure also caused intergranular stress corrosion cracking to occur throughout the bend of the sample. Typical examples of these cracks are shown in Figure 6. Corrosion products (apparently oxides) were observed along the crack walls and the larger second phase was often contained unattached within this oxide.

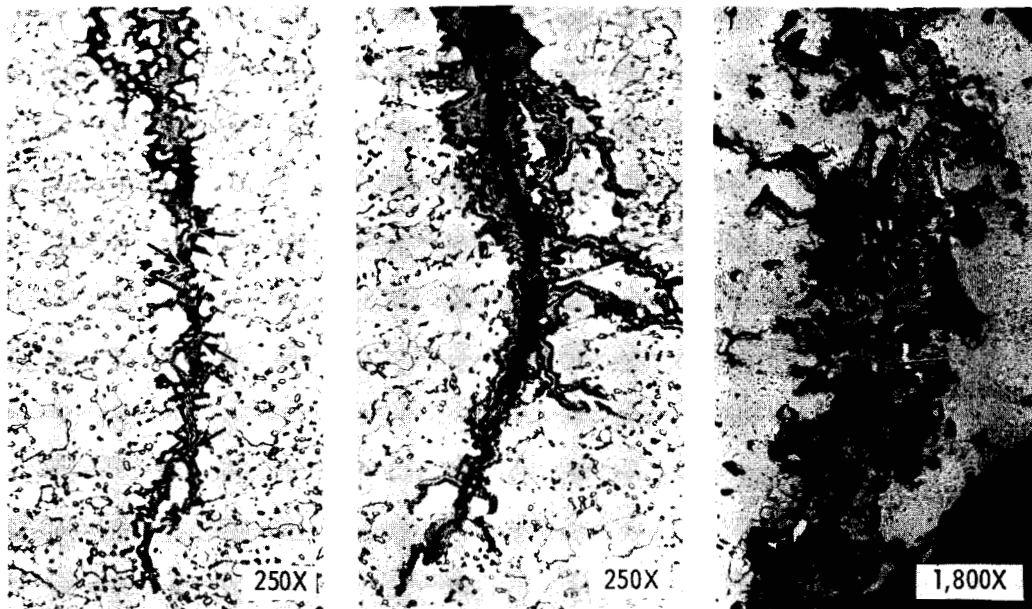
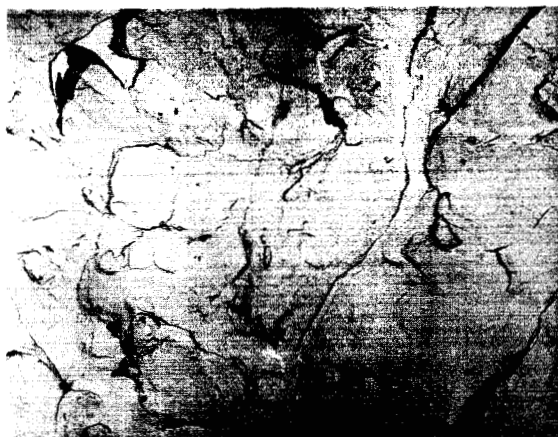


FIGURE 6. TYPICAL STRESS CORROSION CRACKS IN A Ti-8Al-1Mo-1V ALLOY EXPOSED TO DRY SEA SALT AT ELEVATED TEMPERATURES

Second phase is indicated by arrows. Oxide film was on both sides of crack.

After metallographic examination of the sample cross section, the specimen was mechanically fractured in regions containing stress corrosion cracks and in regions remote from the cracks. The fracture faces were then examined by fractographic techniques. This examination indicated that the exposure did not embrittle the sample except for the reduction in cross section caused by the cracks. In regions remote from the cracks, fracture occurred by ductile mechanisms, as shown by the dimpled regions seen in Figure 7a; no evidence of brittle fracture was found. In the region containing stress corrosion cracks, fracture also occurred by ductile mechanisms in the area below the crack tips (Figure 7b). In contrast, the faces of the stress corrosion cracks were characterized by a structure with features approximately the same size as the alpha grains of the alloy (Figure 7c). The detail of these faces indicated that stress corrosion cracking occurred by chemical, not mechanical, means. No evidence of ductile rupture was apparent except near the crack tips where a transition from stress corrosion to mechanical fracture occurred (Figure 7d). One interesting feature of the crack faces was the occurrence

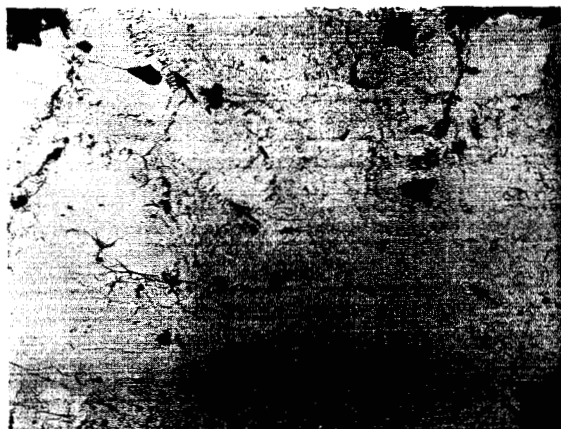
of small secondary cracks that formed patterns of regular striations in isolated areas (see arrows in Figure 7c). The size and orientations of these cracks corresponded to the size and orientation of the fine second phase in the duplex-annealed alloy, indicating that this phase (or the phase boundary) may be involved in the cracking processes. Although these observations have been made on only one sample and their reproducibility and significance have not been confirmed, they show that fractography and structural observations should be useful tools in determining the nature of the susceptible path for stress corrosion cracking. Additional studies are planned along these lines.



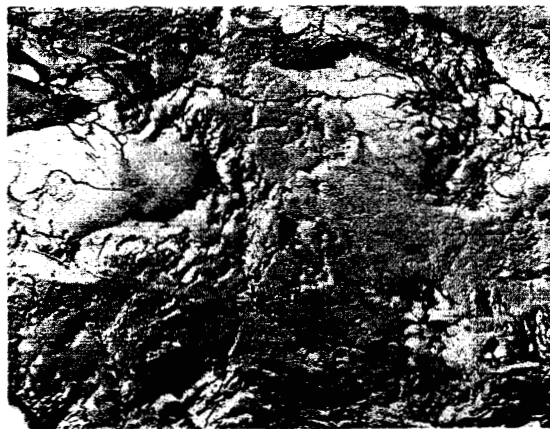
a) Ductile fracture in region remote from cracked area. Note dimpled surface. 3,600X



b) Ductile fracture in region below stress corrosion crack tip 3,600X



c) Stress corrosion fracture face. Arrows indicate secondary cracks. 3,600X



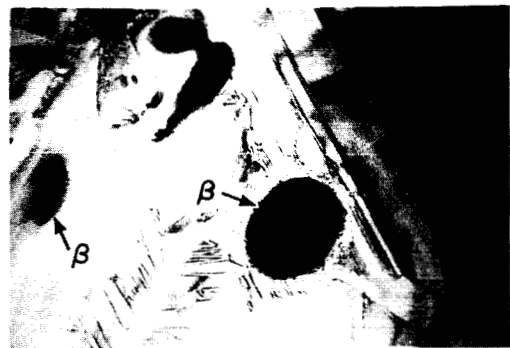
d) Area that failed at crack tip by stress corrosion cracking and mechanical rupture 3,600X

FIGURE 7. FRACTURE DETAIL OF STRESS CORROSION CRACKS AND MECHANICAL RUPTURE IN U-BEND SAMPLE

Thin foils of titanium alloy for electron transmission studies of the fine structure were prepared in a  $\text{HNO}_3$ -HF-lactic acid bath while the sample was under an impressed cathodic current. Study of the effect of fine structure on susceptibility to stress corrosion cracking is proceeding. Figure 8 shows several transmission photographs of the alloy in the mill-annealed condition. Electron diffraction patterns were made from the foils, but indexing of the patterns has not been completed. Therefore, positive interpretations of structural details revealed by these transmission electron-micrographs cannot be given at this time. However, the micrographs reveal an apparent grain boundary (Figure 8a), dark spots (Figure 8b and 8c) that are probably beta phase particles, and some structural detail of the alpha matrix (Figure 8d). These structural features may be due to formation of a super lattice, which is known to occur in the alpha phase in Ti-Al alloys<sup>(2)</sup>, to twinning of the hexagonal structure, or to incipient precipitation along stacking faults. These photographs provide further evidence that the beta phase is cathodic to the matrix, because during thinning of the foils, preferential attack occurred around the edges of the dark spots (beta particles) (Figure 8c).



a) Apparent grain boundary runs diagonally between arrows 21,000X



b) Section shows second phase, probably beta, in the matrix 15,800X



c) Preferential attack at probable alpha-beta interface 21,800X



d) Structural detail of alpha matrix 33,000X

FIGURE 8. TRANSMISSION MICROGRAPHS OF Ti-8 Al-1 Mo-1V ALLOY IN THE MILL-ANNEALED CONDITION

# DESCRIPTION OF ATTACK ON TITANIUM - SEA SALT "SANDWICHES"

Temp, °F	Time Interval, hours	Observations (no microscopy used)
400	0-8	No visible evidence of reaction.
650	0-1	Polished metal surfaces filmed with gold-colored oxide.
650	1-8	No change. No salt-metal reaction visible.
800	0-1	Polished metal surfaces filmed with dull, gold-colored oxide.
800	1-8	Visible evidence of salt-metal (or salt-metal oxide) reaction, with thin layer of reaction products spreading over polished metal surface.
900	0-1	Same as 800°F test, except reaction started within 1 hour.
900	1 to 1-1/2	Reaction continued, with products spreading over polished metal surfaces.
900	2-1/2 to 8	Very little change. Corrosion products near salt-metal interface were white and grey and the surrounding metal was filmed with a blue oxide.
1000	0-1	Reaction started and products began spreading over polished metal surface. Blue oxide on surface surrounded corrosion products.
1000	1-4	Reaction products near salt-metal interface were black with "lava-like" surface as though products were viscous molten forms.
1000	4-8	"Lava-like" products extended entirely across the polished section and began spreading down the outer surface of one sheet. Corrosion products were mixed white, black, and grey with some areas on the metal surface filmed with a blue oxide.
1100	0-1	White and grey corrosion products spread from the salt-metal interface and extended entirely across the polished surfaces. Surrounding metal was filmed with a blue oxide.
1100	1 to 2-1/2	White products converted to grey color with "lava-like" surface appearance.
1100	2-1/2 to 4	A black product appeared near the salt-metal interface.
1100	4-8	"Lava-like" products extended across surfaces on both sheets and began spreading down outer surfaces.
1200	4-8	Same as 1100°F test except that products spread over larger area and more products were produced.



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